

Boundary conditions for molecular dynamics

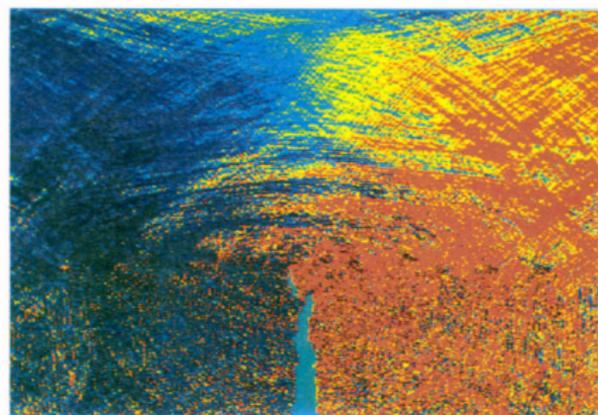
Xiantao Li

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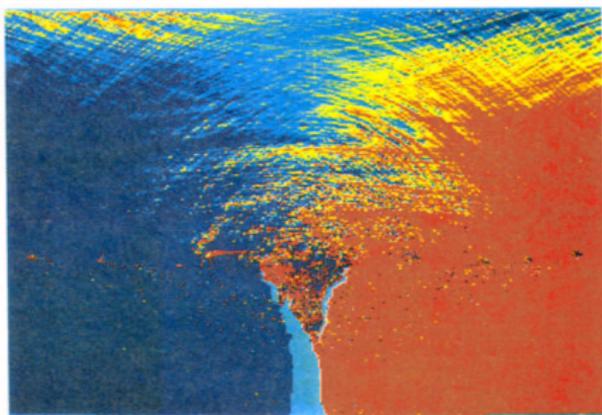
Collaborators

Weinan E and Jerry Z. Yang
Princeton University

Boundary Reflection



(a)



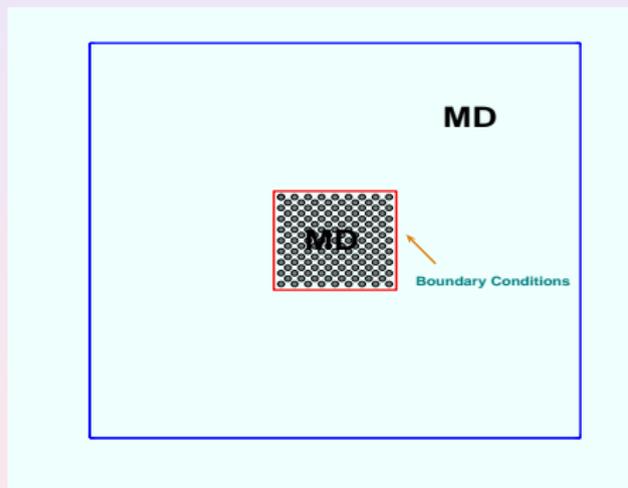
(b)

Fracture simulation in triangular lattice (Holian et. al. 1996)

Boundary condition

The role of boundary conditions:

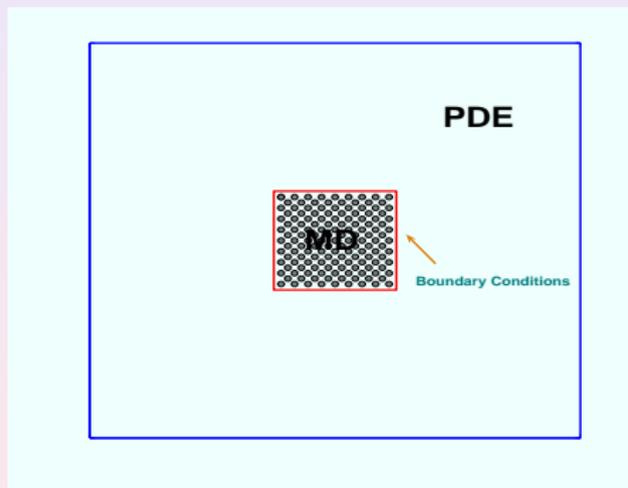
1. Prevent phonon reflection
2. External loading
3. Maintain the system temperature
4. Couple with continuum models



Boundary condition

The role of boundary conditions:

1. Prevent phonon reflection
2. External loading
3. Maintain the system temperature
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Outline

- ▶ General formulation
- ▶ Zero temperature boundary conditions
- ▶ From zero temperature to finite temperature
- ▶ Summary

Mori - Zwanzig's view

Generalized Langevin equation (GLE),

$$\frac{d\mathbf{A}}{dt} = i\omega(t)\mathbf{A} - \int_0^t \Theta(t-s)\mathbf{A}(s)ds + R(t).$$

- ▶ $\mathbf{A} = (\mathbf{q}, \mathbf{p})$: smaller number of variables
- ▶ $\Theta(t)$: correlation matrix
- ▶ $R(t)$: from unresolved degrees of freedom
- ▶ $\langle R(t)A(0) \rangle = 0$

Random forcing

For system embedded in a linear heat bath,
 $R(t)$ is a stationary Gaussian process.

The second fluctuation dissipation theorem:

$$\langle R(t)R(0)^T \rangle = \langle p(0)^2 \rangle \Theta(t) = k_B T \Theta(t).$$

- ▶ the correlation function determines the random force
- ▶ for $T = 0$, $R = 0$; $\Theta(t)$ provides zero temperature BC.

Existing work

GLE formulations

One dimensional case: Adelman and Doll 1974, 1975

Multi dimensional case: Tully 1980

...

Zero temperature BC

Exact BC: Cai, de Koning, Bulatov and Yip 2000

Approx. BC: E and Huang 2001, 2002

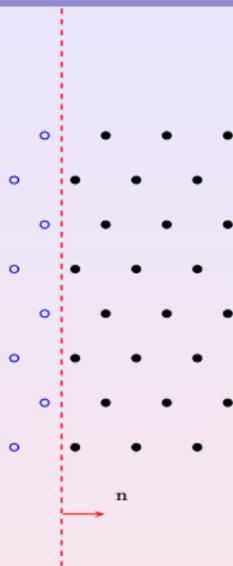
General Exact BC: Wagner, Karpov, Liu, Park et al 2004, 2005

Approx. BC for general system: E and Li 2006

Zero temperature boundary condition

Exact boundary conditions:

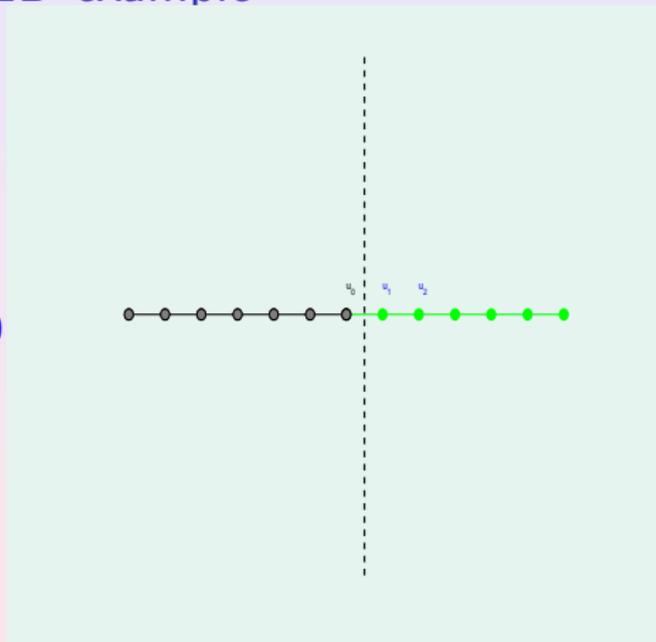
$$\mathbf{u}_i(t) = \sum_j \int_0^t \theta_j(s) \mathbf{u}_{i+j}(t-s) ds.$$



Boundary condition

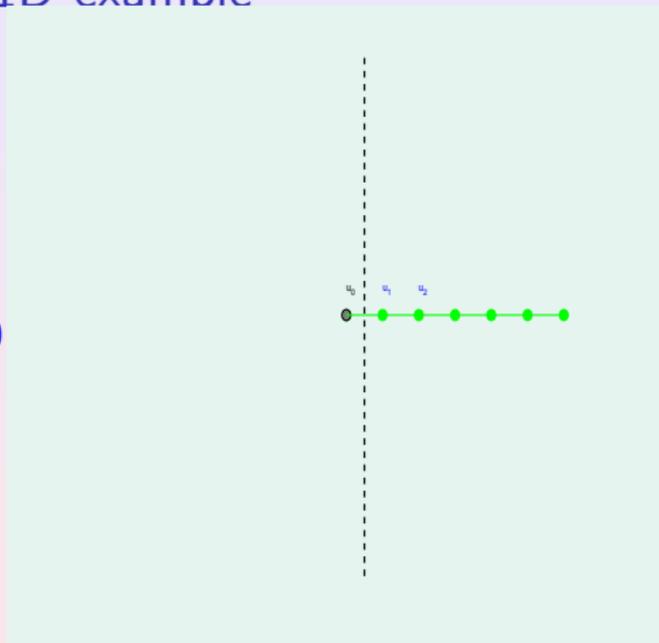
Exact boundary condition: a 1D example

$$u_0(t) = \int_0^t \beta(t-s)u_1(s)ds, j \leq 0$$
$$\beta = \frac{J_2(2t)}{t}$$



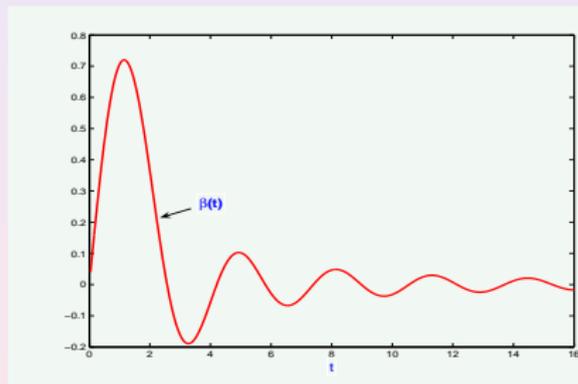
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Boundary conditions: exact vs approximate

Exact boundary conditions:

- ▶ **nonlocal** in both space and time
- ▶ numerical implementation is expensive
- ▶ premature truncation leads to large reflection

Local boundary condition:

Variational BC (E and Huang 2001 and 2002, E and Li 2006)

$$\mathbf{u}_i(t) = \sum_{j \in J} \int_0^{t_0} A_j(s) \mathbf{u}_{i+j}(t-s) ds, \quad |J| \text{ finite.}$$

- ▶ Local in both space and time
- ▶ Minimize phonon reflection
- ▶ Optimal on a given stencil (J and $(0, t_0)$)

Variational boundary condition

Main components:

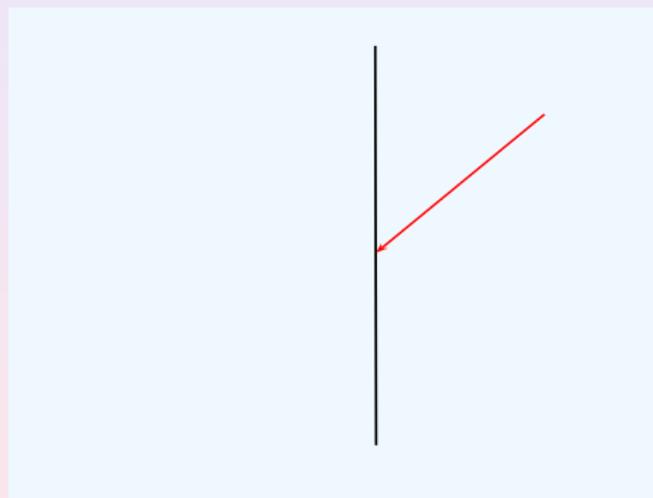
1. Reflection coefficients
2. Energy flux
3. Variational formulation

$$\begin{aligned} \mathbf{u}_j &= e^{i(\mathbf{r}_j \cdot \mathbf{k}^I - \omega_s t)} \boldsymbol{\epsilon}_s(\mathbf{k}^I) \\ &+ c_{ss'}^R e^{i(\mathbf{r}_j \cdot \mathbf{k}^R - \omega'_s(\mathbf{k}^R) t)} \boldsymbol{\epsilon}'_s(\mathbf{k}^R) \end{aligned}$$

Variational boundary condition

Main components:

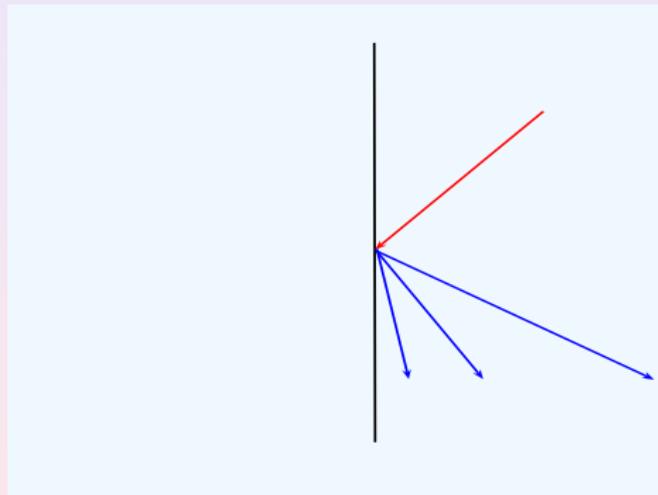
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Variational boundary condition

Main components:

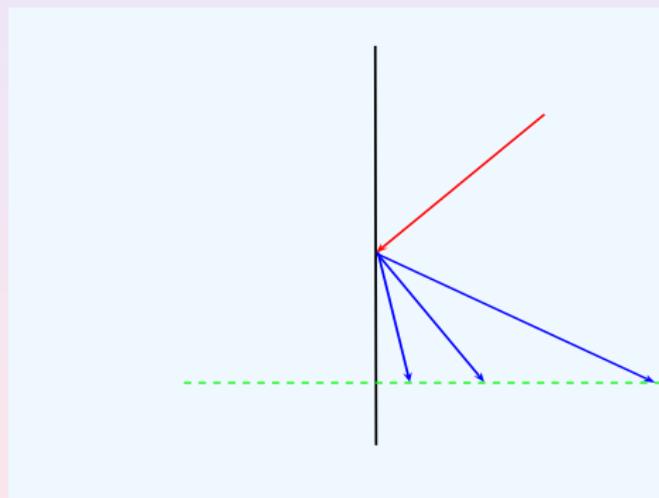
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Variational boundary condition

Main components:

1. Reflection coefficients
2. Energy flux
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Variational boundary condition

Main components:

1. Reflection coefficients
2. Energy flux
3. Variational formulation

$$J_R = \sum_s \int_{BZ} \left| \sum_l c_{ss'l}^R \right|^2 \omega_s^2 (\nabla \omega_s \cdot \mathbf{n}) dk.$$

Variational boundary condition

Main components:

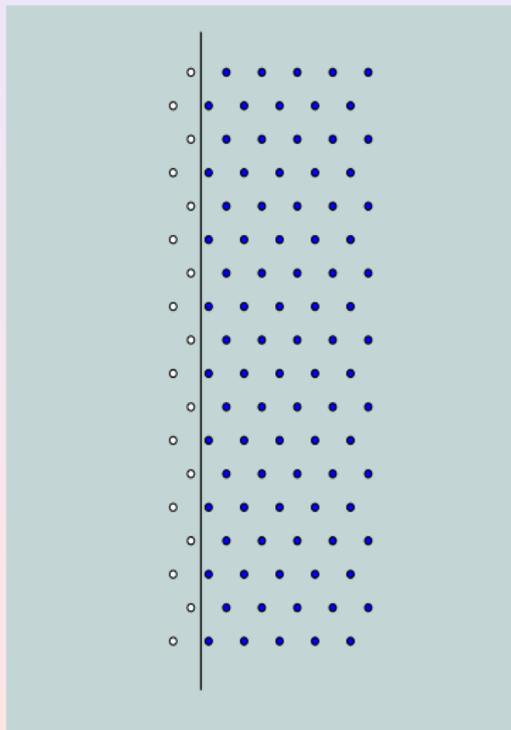
1. Reflection coefficients
2. Energy flux
3. Variational formulation

$$\begin{aligned} & \min_{\{\alpha_j\}} I[\{\alpha_j\}; \mathbf{n}] \\ \triangleq & \sum_s \int_{BZ} \sum_l |c_{ss'l}^R|^2 (\nabla \omega_s \cdot \mathbf{n}) d\mathbf{k} \end{aligned}$$

Choosing the stencil J

The space stencil J ,

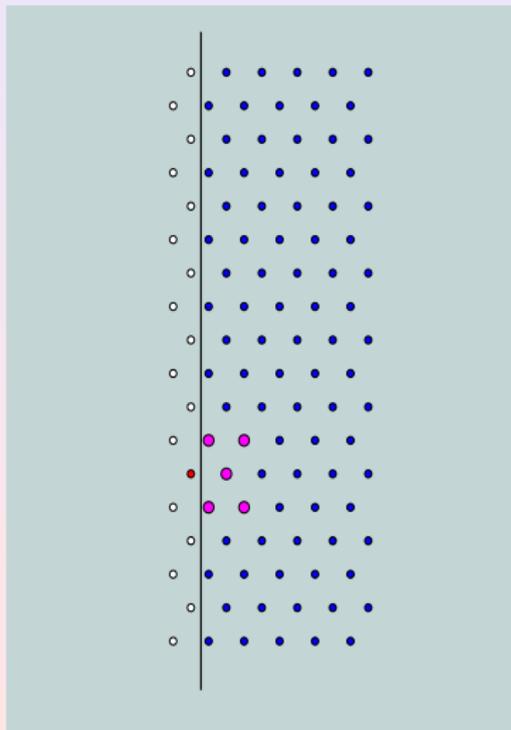
- ▶ only involves a small number of atoms
- ▶ translational invariant along the boundary
- ▶ respect some crystal symmetry



Choosing the stencil J

The space stencil J ,

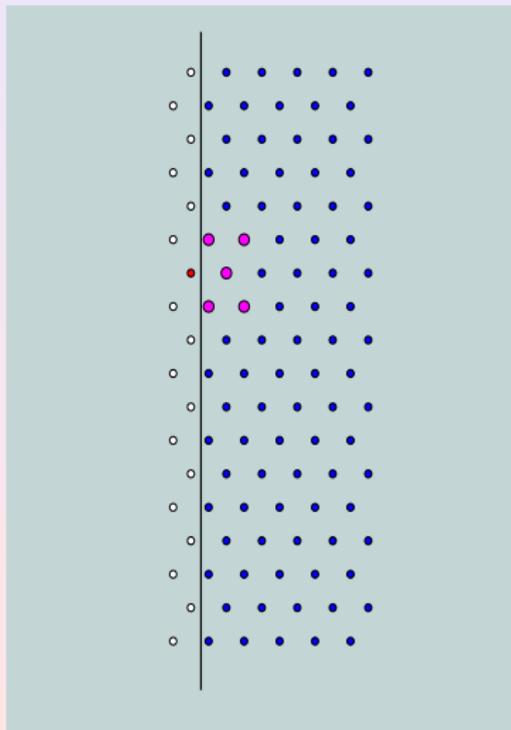
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Choosing the stencil J

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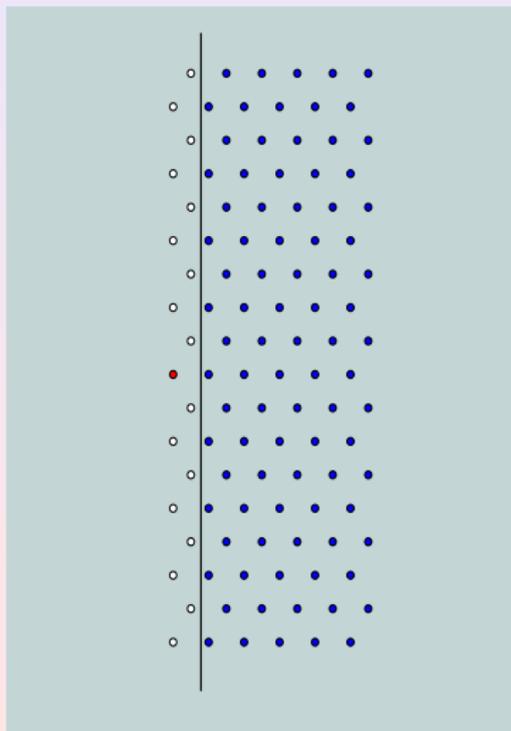
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Choosing the stencil J

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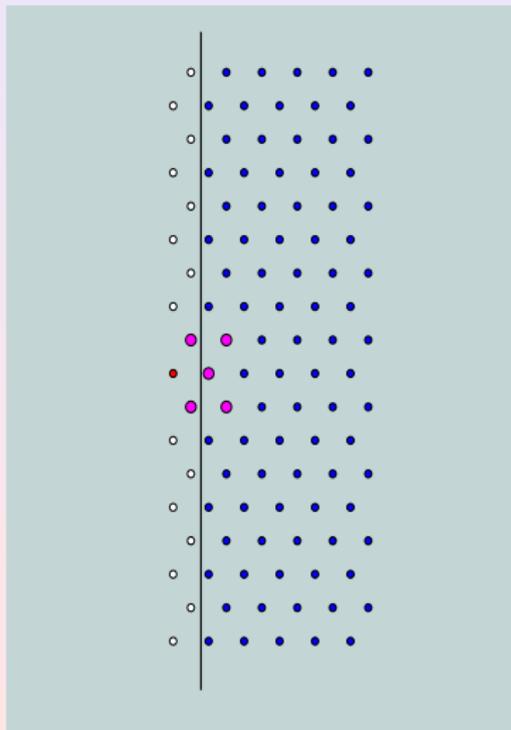
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Choosing the stencil J

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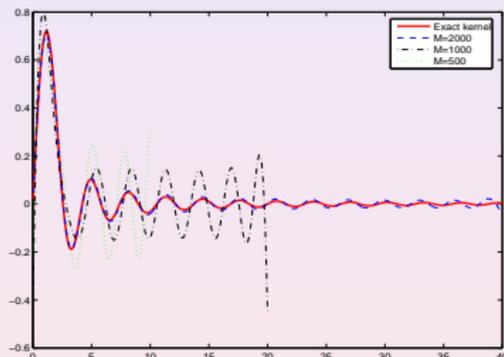
- ▶ only involves a small number of atoms
- ▶ translational invariant along the boundary
- ▶ respect some crystal symmetry



Example I: 1D chain

$$R(k) = \frac{1 - \sum_j e^{ijk} \int_0^{t_0} a_j(\tau) e^{i\omega\tau} d\tau}{1 - \sum_j e^{-ijk} \int_0^{t_0} a_j(\tau) e^{i\omega\tau} d\tau}.$$

- ▶ The approximate kernels can be quite different from the exact ones
- ▶ VBC leads to much less reflection than the exact BC truncated to the same interval

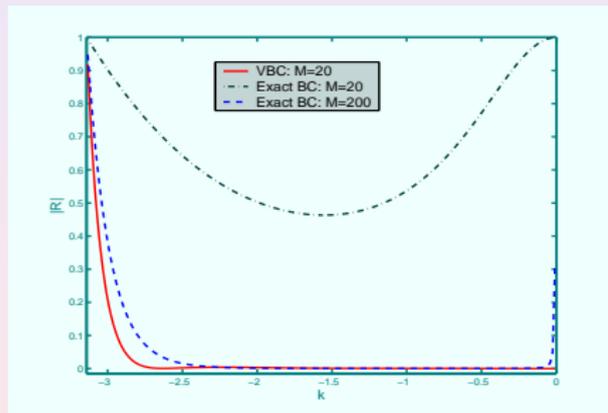


time history kernels

Example I: 1D chain

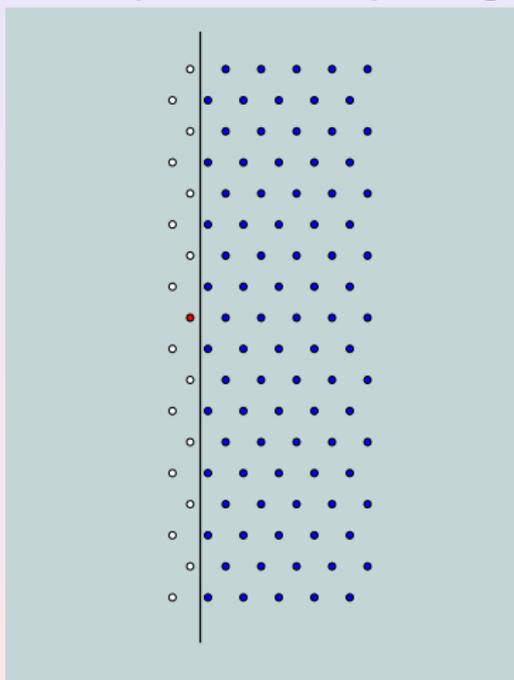
$$R(k) = \frac{1 - \sum_j e^{ijk} \int_0^{t_0} a_j(\tau) e^{i\omega\tau} d\tau}{1 - \sum_j e^{-ijk} \int_0^{t_0} a_j(\tau) e^{i\omega\tau} d\tau}.$$

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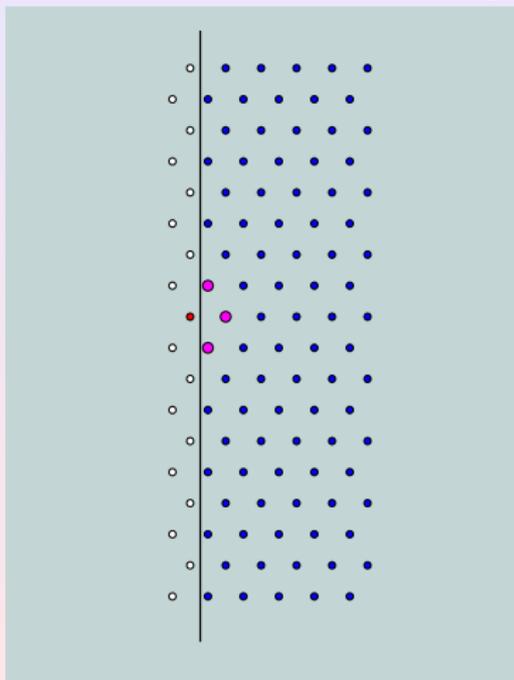
phonon reflection

Example II: comparing different stencils



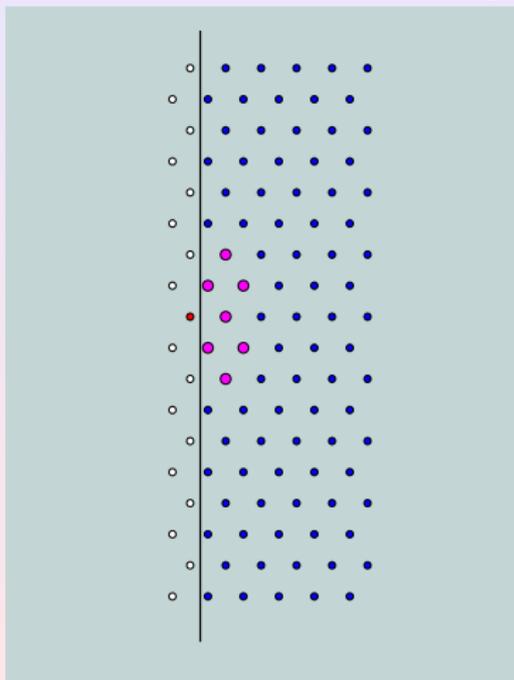
Selection of the stencil

Example II: comparing different stencils



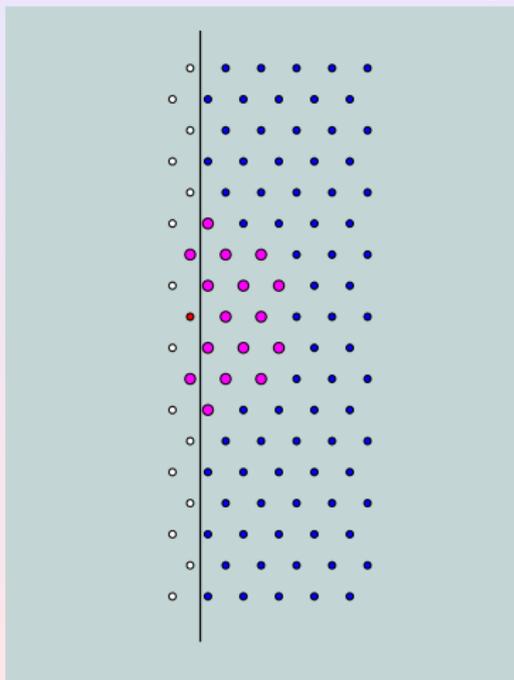
$$|J| = 4$$

Example II: comparing different stencils



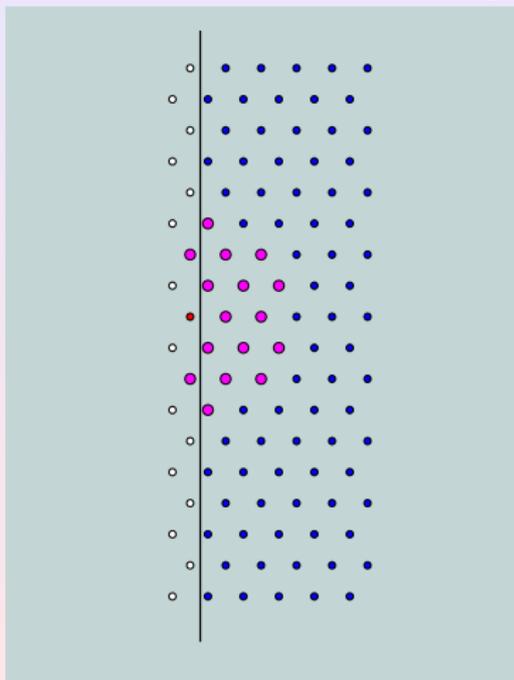
$$|J| = 8$$

Example II: comparing different stencils

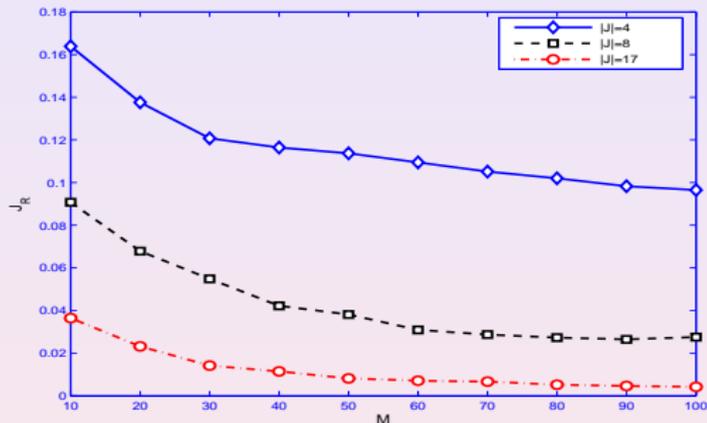


$$|J| = 17$$

Example II: comparing different stencils



$$|J| = 17$$



Total reflection on various stencil

Application: fracture simulation in BCC Iron

fixed boundary condition

variational boundary condition



From zero to finite temperature: GLE

Boundary condition:

$$\mathbf{U}(\mathbf{r}, t) = \sum_j \int_0^t A_j(t-s) \mathbf{u}(\mathbf{r} + \mathbf{r}_j, s) ds.$$

- ▶ $\mathbf{r} \in J_0$ the boundary atoms — those atoms at the boundary that have been removed from the system,
- ▶ $\mathbf{r} + \mathbf{r}_j \in J_1$: the interior atoms next to the boundary that are directly influenced by the boundary atoms.

For $\mathbf{r} \in J_1$,

$$\mathbf{f}(\mathbf{r}, t) = -\frac{\partial V}{\partial \mathbf{r}} + \mathbf{f}^{\text{ex}},$$

\mathbf{f}^{ex} : the force due to the boundary atoms,

$$\mathbf{f}^{\text{ex}} = \sum_{\mathbf{r}_k \in J_0} D_k U(\mathbf{r}_k, t).$$

Zero temperature GLE

Adding the external force:

$$\ddot{\mathbf{u}}(\mathbf{r}, t) = \sum_m \int_0^t \beta_m(s) \mathbf{u}(\mathbf{r} + \mathbf{r}_m, t - s) ds - \frac{\partial V}{\partial \mathbf{r}}.$$

GLE in the standard form,

$$\ddot{\mathbf{u}}(\mathbf{r}, t) = \sum_m \Theta_m(0) \mathbf{u}(\mathbf{r} + \mathbf{r}_m, t) - \int_0^t \Theta_m(s) \dot{\mathbf{u}}(\mathbf{r} + \mathbf{r}_m, t - s) ds - \frac{\partial V}{\partial \mathbf{r}} + R(t)$$

$$\Theta_m(t) = - \int_t^\infty \beta_m(s) ds.$$

Solving GLE

Represent the noise by a Fourier integral:

$$R(t) = \int \hat{R}(\omega) e^{i\omega t} d\omega.$$

The Fourier coefficients are Gaussian random variables and,

$$\langle R(t)R(0)^T \rangle = \Theta(t) \implies \langle \hat{R}(\omega)\hat{R}(\eta) \rangle = \hat{\Theta}(\omega)\delta(\omega + \eta).$$

- ▶ $\hat{\Theta}(\omega)$: power spectrum
- ▶ the random noise is determined by the power spectrum

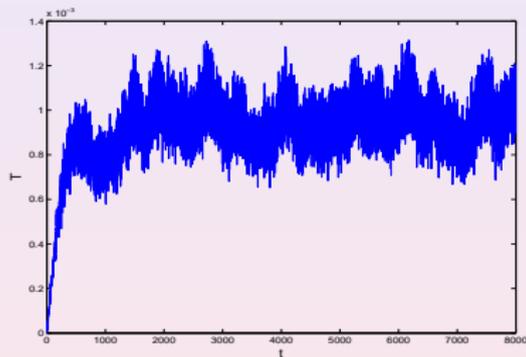
Approximation of the power spectrum

$$\hat{\Theta} - \hat{\Theta}_0 \sim C(E + C\tilde{E})^{-1}.$$

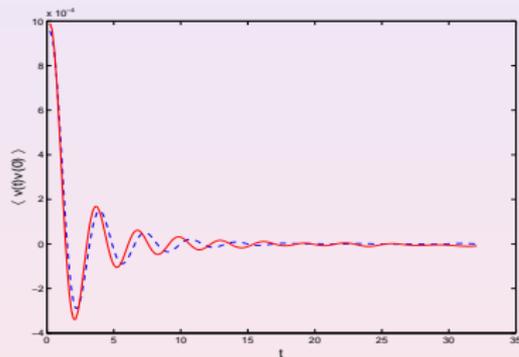
- ▶ Θ : computed from approximate boundary condition
- ▶ Θ_0 : computed from exact boundary condition
- ▶ C : reflection coefficients.

The error is controlled by the reflection coefficients !

Example I: one dimensional chain

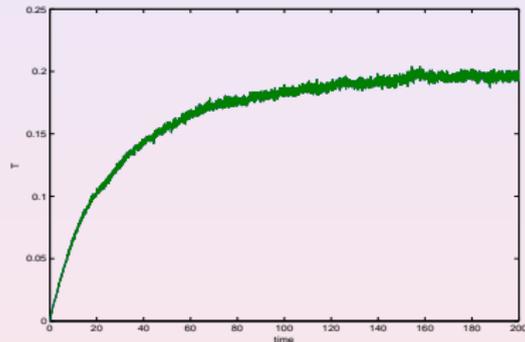


System temperature

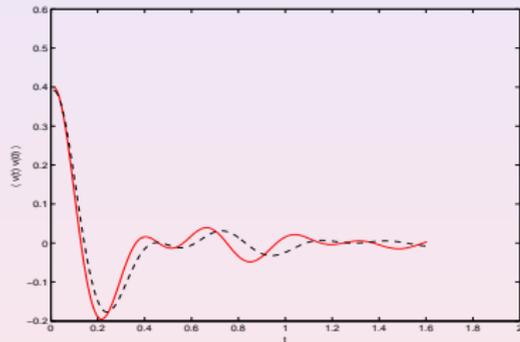


Velocity correlation

Example II: 2D triangular lattice



System temperature



Velocity correlation

Summary

1. General formulation from Mori - Zwanzig's viewpoint
2. Determine the random forcing from the correlation function
3. Variational formulation to obtain the correlation function
4. Reflection coefficients as a measure of the accuracy
5. Applications to various systems

Reference: X. Li and W. E, Variational boundary conditions for molecular dynamics simulations of solids at low temperature, *comm. comp. phys.* **1** (2006), 136--176.